ALKYLATION OF NITROPARAFFINS WITH AMINES AND THEIR DERIVATIVES

BY

WILLIAM EARL HAMLIN

B.A., Lawrence College, 1944
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

ALKYLATION OF NITROPARAFFINS WITH AMINES AND THEIR DERIVATIVES

BY

WILLIAM EARL HAMLIN

B.A., Lawrence College, 1944
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor H. R. Snyder for suggesting this study and for his advice and encouragement during its prosecution.

The author is also indebted to the University of Illinois for teaching assistantships during the years 1947-1948 and 1948-1949.

ALKYLATION OF NITROPARAFFINS WITH AMINES AND THEIR DERIVATIVES

Introduction

The recent commercial availability of the simple nitroparaffins has stimulated their investigation as intermediates in the production of other synthetic organic chemicals. Although the simple nitroparaffins have a reactive methylene group capable of entering into many of the reactions characteristic of the methylene group of ketones, no general procedure for carbon-alkylation of nitroparaffins has yet been developed. Recently certain amines have been employed for the alkylation of simple nitroparaffins. These reagents all have been amines of the Mannich base type; it is possible that they have served as sources of unsaturated compounds and that the apparent alkylations really have been condensations of the Michael type.

The present investigation was undertaken to determine whether amines and quaternary ammonium salts not structurally capable of forming unsaturated compounds for condensations of the Michael type can be used to alkylate nitroparaffins, and to search for other nitrogen-containing reagents for use in such alkylations.

Discussion Of Results

Benzyl quaternary ammonium salts which alkylate active methylene compounds by an apparent S_N2 mechanism (1) have been shown not to alkylate nitroparaffins. When an aqueous solution of benzyldimethylphenylammonium chloride was refluxed with an equimolar quantity of the sodium salt of 1- or 2-nitropropane benzaldehyde and dimethylaniline were obtained.

Ketonic Mannich bases alkylate nitroparaffins presumably by amine elimination to form unsaturated compounds followed

by 1,4-addition of the nitroparaffins. The reaction of β-dimethylaminopropiophenone with nitromethane (2) was extended to the two nitropropanes. The alkylation of 1-nitropropane yielded a liquid which decomposed on distillation and could not be identified, but 2-nitropropane was easily alkylated to yield a white low-melting solid.

Phenolic Mannich bases can be considered as enol forms of the ketonic bases and would be expected to alkylate nitroparaffins. α-Dimethylaminomethyl-β-naphthol (3) did not alkylate 1-nitropropane, but formed di-(2-hydroxy-1-naphthalene)-methane by self-condensation, a reaction which also occurs when the Mannich base is heated with dilute alkali (4). When a mixture of *o*- and *p*-dimethylaminomethylphenol was heated with 1-nitropropane a resin was formed, but no alkylated product was detected.

The Mannich bases of 1-nitropropane, N-(2-nitrobutyl)-diethylamine (5) and N-(2-nitrobutyl)-dimethylamine, can alkylate nitroparaffins according to a mechanism similar to that proposed for ketonic Mannich bases. These reagents have been used to alkylate 1-nitropropane and 2-nitropropane and the corresponding dinitro compounds have been catalytically reduced to the diamines. The ethyl and methyl cyanoacetic esters have also been alkylated. N-(2-Nitrobutyl)-dimethylamine readily underwent amine exchange when refluxed with excess piperidine, but the reaction was accompanied by considerable polymerization. The methiodide of N-(2-nitrobutyl)-diethylamine could not be prepared.

N-(2-Nitroisobutyl)-dimethylamine (6) cannot form an unsaturated intermediate by amine elimination and would not be expected to alkylate nitroparaffins. Its unreactivity was confirmed by an attempted alkylation of 2-nitropropane. No alkylated product was detected. The Mannich base did not undergo amine exchange with piperidine, but when its hydrochloride was refluxed with excess piperidine a trace of N-(2-nitroisobutyl)-piperidine was detected by means of its picrate derivative.

The Mannich base of 2-nitropropane readily formed a methiodide which was tested for alkylating properties; carbon-alkylation of acetaminocyanoacetic ester and oxygen-alkylation of α-naphthol were not observed.

Benzyldialkylamine oxides resemble the benzyl quaternary ammonium salts in their salt-like properties and could conceivably serve as alkylating agents. Since benzyl quaternary ammonium salts have been shown to be incapable of alkylating nitroparaffins, it is not suprising that benzyldiethylamine oxide failed to alkylate 1-nitropropane. Benzyldimethylamine oxide failed to alkylate acetaminocyanoacetic ester, and the oxide was not cleaved by aqueous sodium hydrosulfite or sodium sulfide. When a diethylene glycol solution of sodium sulfide hydrate was employed the oxide was reduced to benzyldimethylamine.

Benzyldimethylamine oxide methiodide was found to be a little more reactive than the corresponding oxide. Although the quaternary salt failed to alkylate acetaminocyanoacetic ester or thiophenol, it was found to undergo cleavage to a slight extent when heated with a diethylene glycol solution of sodium sulfide hydrate. Benzyl sulfide was isolated and a very volatile liquid, presumably methyl sulfide or methyl mercaptan, was observed.

This investigation has revealed no exception to the proposal that alkylation of nitroparaffins by amines must proceed through an elimination-addition mechanism.

BIBLIOGRAPHY

1. Snyder and Brewster, J. Am. Chem. Soc., 71, 291 (1949).
2. Reichert and Posemann, Arch. Pharm., 275, 67 (1937).
3. German Patent 89979; Frdl., 4, 99 (1899).
4. Auwers and Dombrowski, Ann., 344, 280 (1906).
5. Blomquist and Shelley, J. Am. Chem. Soc., 70, 147 (1948).
6. Johnson, *ibid.*, 68, 12 (1946).

VITA

The author was born in Wautoma, Wisconsin, on July 3, 1922. He attended the public schools of Highwood and Highland Park, Illinois, and was graduated from the Highland Park High School in June, 1940. He entered Lawrence College in September, 1940, and was granted the Bachelor of Arts degree in February, 1944. He entered the Naval School of Oriental Languages, University of Colorado in April, 1944, and was graduated as a Chinese interpreter in September, 1945. After service in China he was released from active duty in August, 1946. The following month he entered the Graduate College of the University of Illinois where he received his Master of Science degree in September, 1947. He held part-time teaching assistantships in the academic years 1947-1948 and 1948-1949.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549807_0069